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USE OF MODERN MATERIALS FROM GEOKOM CO. FOR PRODUCTION OF CERAMIC WARE

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A comparative analysis of the quality of current materials for the ceramics industry manufactured by domestic and foreign manufacturers is given. The high effectiveness of using modern high-quality materials from GEOKOM Co. in manufacturing ceramics is demonstrated. Information is reported on the effective use of wollastonite, calcite, talc, and kaolin in production of different ceramic ware.

Different raw materials have now been proposed for production of modern ceramic ware.

The lack of a unified system of materials quality indexes and the use of different standards, methods and instrumental bases for measurements complicate making an objective decision in selecting an appropriate brand of material. The main cause of misunderstandings is different versions of the terms used in technical or advertising materials, characteristics, indexes, and methods of determining them.

The currently used instruments for determining particle size frequently produce important differences in measuring the same samples. This is due to both different methods of measurement (sedimentation, diffraction, optical, etc.) and the features of the instruments from different companies, although they are of the same type (principle of measurement).

Another very important characteristic of fillers is the set of spectral coloristic indexes (SCI) of a material – whiteness, brightness, reflection factor, luminosity, yellowness, and color coordinates. Despite the fact that determination of SCI is solely instrumental, standardized by international agreements, and the abundance of externally similar indexes also frequently causes confusion.

As a manufacturer of many mineral fillers, including raw-material components for production of modern ceramic ware, GEOKOM Co. is interested in the correct and competent interpretation of information and in the unbiased comparison of such materials from other companies.

For this purpose, GEOKOM specialists regularly conduct studies of materials of the same type from different manufacturers and publish their findings in the press and on the company's web site, www.geokom.com.

The certified instrumental-analytical and methodological base used in the studies remains the same for analyzing all samples, which allows making valid comparisons. The basic

indexes of microwollastonite and microtalc manufactured in different countries are reported in Tables 1 and 2.

Active conversion to raw materials of higher quality has been observed in recent years. This is greatly due to the attempt of manufacturers to make their products more attractive and increase their competitiveness. The large Western manufacturers (Omya, Luzenac, Imerys, Huber, etc.) play an important role here, as they have especially introduced high-tech brands of their products.

Of the high-quality materials manufactured by GEOKOM for production of modern ceramic ware, such materials as wollastonite, trademark MIVOLL[®]; talc – MITAL[®]; calcite – MIKARB[®]; kaolin – MIKAO[®] should be mentioned. All of these materials are distinguished by high stability of the physicochemical indexes regulated in production of modern ceramic ware. These are primarily the chemical composition with 95–99% basic substance and guaranteed by a low content of chromophoric impurities, and high dispersion and spectral-coloristic properties.

MIVOLL[®] wollastonite is a natural calcium metasilicate (TU 5777-006-40705684–2003), is not carcinogenic (CAS N13983-17-0 group 3), is a fluffy white powder, does not dissolve in water, and has a microneedle structure. This structure greatly determines the area of application of wollastonite in ceramics.

Typical Characteristics of MIVOLL[®] Wollastonite

Density, g/cm ³	2.9
Refractive index.	1.63
SIELab whiteness (ISO 787/1, C/2°), %	95–97
ISO 2470 brightness (R_{457}), %.	88–90
pH of aqueous solution	9–10
Mohs hardness	4.5 (like feldspar)
TCLE, °C.	6.5×10^{-6}
Particle size (D_{50} for different brands), μm	2–50
Characteristic ratio (ratio of the particle length to the diameter)	3–30

¹ GEOKOM CJSC, Polotnyaniy Zavod, Kaluga oblast, Russia; Stroipolimerkeramika OJSC, Vorotynsk, Russia.

TABLE 1

Index	NORDKALK PARTEK, Finland			NYCO Mi- nerals, Inc. NYGLOS-8, USA	ALDERO Wollastonite WTN 60, Italy	GEOKOM Co., MIVOLL®					
	FW-200	FW-325	WIC-10			30-97	30-96	10-97	10-96	05-97	03-97
Mass fraction, %:											
CaO	44	44	44	46	46	46	46	46	46	46	46
SiO ₂	53	53	53	52	51	52	52	52	52	52	52
Fe ₂ O ₃	0.15	0.15	0.15	0.80	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Calcination loss (100°C, 1 h), %	0.9	0.9	0.9	0.5	1	1	1	1	1	1	1
Characteristic ratio	3 : 1	3 : 1	8 : 1	19 : 1	3 : 1	10 : 1	4 : 1	16 : 1	5 : 1	20 : 1	6 : 1
Residue on No. 0045 sieve, %	10.00	2.00	0.10	0.80	10.00	24.00	1.00	0.10	0.02	0.05	0.01
Median particle diameter, µm:*											
maximum D_{98}	111	104	12	100	91	120	90	90	55	60	23
minimum D_{10}	1.8	1.6	1.3	1.5	2.1	4.0	3.5	2.5	2.0	2.0	1.5
Average particle diameter D_{50} , µm:											
median*	16.0	14.0	4.0	7.5	18.0	31.0	26.0	10.0	10.0	5.2	2.8
manufacturer's data (Sedigraph/CILAS)	18	13	4.5	8	—	—	—	—	—	—	—
Evaluation of color characteristics:											
CIE Lab whiteness (ISO 787/1, C/2°), %	95.7	95.0	95.0	97.0	96.4	96.0	95.5	97.2	96.0	97.4	96.6
CIE Lab L lightness, %	95.8	95.4	95.5	97.3	96.7	96.3	96.0	97.3	96.0	97.5	96.6
DIN 53163 brightness (Ry, C/2°), %	89.0	88.5	90.0	92.5	91.7	90.8	88.0	93.3	89.0	94.0	91.6
ASTM D1925-70 yellowness (C/2°), %	3.0	3.8	3.9	4.0	3.1	3.0	2.5	2.4	2.5	2.4	2.0
ISO 2470 brightness (R_{457}), %	87.0	86.4	88.0	90.0	90.0	89.7	87.0	92.6	88.0	93.6	92.0
ISO 11475 whiteness ($D_{65}/10^\circ$), %	81.5	79.9	80.0	85.0	85.1	84.0	81.5	90.0	83.0	91.0	90.0
ISO 787/5 oil absorption, g/100 g	18	22	42	44	19	25	23	34	30	39	45

* Measured on a Microsizer-201A.

Since it has a needle structure, wollastonite is a micro-reinforcing element in ceramic pastes.

Studies and industrial tests demonstrated its advantages in comparison to other materials traditionally used in ceramic pastes, glazes, engobes, etc.

For example, experimental work has been conducted at Stroipolimerkeramika Co. on selecting ceramic pastes that would improve sintering of sanitary and construction articles to decreased the firing temperature in zones with the maximum temperature. It was necessary to develop a new blend composition with optimum slip casting properties, improved chemical composition and sedimentation properties, sensitivity to drying, and resistance to deformation.

Of all formulas tested, a positive result was obtained using calcium flux in the ceramic paste – MIVOLL® wollastonite. The experimental composition was tested in production conditions. The amount of wollastonite in the paste was approximately 2%.

The following conclusions can be drawn from the results obtained: the casting properties are satisfactory; the physical and chemical properties satisfy the requirements imposed in production of sanitary and construction ware.

All articles were graded and the results are reflected in kerosene control reports and in grading reports. The data on water absorption, shrinkage, and buckling are reported in Table 3.

There was an important decrease in water absorption in articles made from the experimental paste, and elevated deformation resistance of the paste was observed due to the well-developed needle structure of MIVOLL® wollastonite.

After incorporation of the new paste in mass production, the firing temperature decreased by 35–37°C for a firing time of 16–20 h.

The use of ceramic paste containing MIVOLL® thus not only improves the consumer properties of sanitary and construction ware and popular consumer goods but also increases the production process indexes and significantly decreases the firing temperature in furnace zones with the maximum temperature.

The use of MIVOLL® wollastonite in glazes and as partial replacement of calcium carbonate by calcium silicate makes it possible to improve the organoleptic properties of the glazes by reducing the pinholes on the surface of the glaze. Replacement of traditional calcium flux (chalk) by MIKARB® micromarble which does not contain chromophore impurities and particles less than 1 µm in size not only prevents rejections for “glaze shivering” and “bald spot” indexes but also increases the whiteness of the fired article. On the whole, use of these materials increased the glaze whiteness by 5%.

The demand for wollastonite in production of ceramic tiles increased sharply with the introduction of accelerated

TABLE 2

Index	Mondo Minerals Finntalc, Finland					Luzenac Group				GEOKOM MITAL®														
	M50	M30	M15	M05	Micro-Talc A.T.1	Italy		France, Stealen	MICRO-FILL Zeta Talc EW20, Greece	MT-15-99	MT-15-99M	MT-10-95	MT-10-99	MT-07-95	MT-07-99	MT-05-99	MT-15-96	MT-10-80	MT-10-96	MT-07-96	MT-05-96	MT-03-96		
						Talc A7C	Extra 5/0																	
Mass fraction, %:																								
SiO ₂	60	60	60	60	39	58	59	—	—	60	44	60	60	60	60	60	45	40	45	45	45	45	45	
MgO	31	31	31	31	32	31	32	—	—	30	32	32	32	32	32	32	33	32	33	33	33	33	33	
Al ₂ O ₃	—	—	—	—	—	2	2	—	—	—	—	—	—	—	—	—	12	0.2	12	12	12	12	12	
Residue on No. 004 sieve, %	29.00	5.20	0.05	0.01	0.05	0.05	4.20	0.50	0.05	2.40	5.40	0.10	0.10	0.07	0.07	0.01	1.00	0.10	0.10	0.05	0.01	0.00		
Median particle diameter, μm:*																								
maximum <i>D</i> ₉₈	102.0	68.0	27.0	21.0	27.0	26.0	91.5	59.0	30.3	56.0	92.0	32.0	32.0	27.0	27.0	22.0	56.0	33.0	32.0	28.0	24.0	18.0		
minimum <i>D</i> ₁₀	6.9	4.1	2.5	1.6	2.2	1.9	4.8	3.5	2.4	5	5	3	3	2	2	1.5	4.5	2.5	2.5	2	1.5	1		
Average particle diameter <i>D</i> ₅₀ , μm:																								
median*	38.0	15.4	7.2	5.3	6.7	6.1	24.6	15.9	8.3	13.5	13.5	8.5	8.3	6.7	6.1	4.3	14.0	9.2	8.5	6.5	5.0	3.5		
sedimentation (SF-2 photosedimentograph) manufacturer's data (Sedigraph 5100)	—	12.9	7.5	4.4	—	—	—	—	—	14.2	14.2	8.6	8.6	6.9	6.4	4.4	—	—	—	—	—	—		
Evaluation of color characteristics:																								
CIELab whiteness (ISO 787/1, C/2°), %	90.1	91.6	92.9	95.1	91.1	97.4	96.3	98.0	97.8	98.7	98.7	95.5	98.8	95.5	98.8	98.8	95.5	84.0	96.5	96.5	96.5	96.5		
CIELab L lightness, %	90.4	92.0	93.2	95.5	92.0	98.0	97.0	98.5	98.0	98.5	98.5	95.7	99.0	95.7	99.0	99.0	96.0	—	97.0	97.0	97.0	97.0		
DIN 53163 brightness (R _y , C/2°), %	77.0	79.6	82.7	87.9	79.2	93.8	91.3	96.2	95.4	96.5	96.5	89.0	97.0	89.0	97.0	97.0	90.0	—	92.0	92.0	92.0	92.0		
ASTM D1925-70 yellowness (C/2°), %	4.2	3.0	2.5	2.0	3.9	2.2	2.9	3.5	2.8	2.2	2.2	1.5	1.8	1.5	1.8	1.8	3.5	—	3.0	3.0	3.0	3.0		
ISO 2470 brightness (<i>R</i> ₄₅₇), %	75.4	78.5	81.9	88.5	76.7	92.6	89.1	95.5	93.2	94.5	94.5	88.0	96.0	88.0	96.0	96.0	88.5	64.0	90.0	90.0	90.0	90.0		
ISO 11475 whiteness (<i>D</i> ₆₅ /10°), %	66.5	72.8	79.9	84.0	69.5	89.6	85.1	89.9	89.3	91.2	91.2	85.7	93.5	85.7	93.5	93.5	82.3		86.0	86.0	86.0	86.0		
ISO 787/5 oil absorption, g/100 g	23	31	39	47	36	36	29	31	29	25	23	30	30	34	34	43	20	27	25	28	35	44		

* Measured on a Microsizer-201A.

firing processes. Most of the wollastonite consumed is used in production of wall tiles and flooring tiles, sanitary-industrial, and special articles, as well as ceramics made from colored clays, usually to prevent crack formation, high shrinkage, and other defects.

With the startup of automated lines for fast (45 – 70 min), low-temperature firing (950 – 1050°C), traditional tile paste compositions based on argillaceous components and fluxes did not ensure a contemporary level for the properties of the tiles even on addition of up to 15% nonplastic raw material (chalk, marble, talc, quartz, etc.). High shrinkage and consequently high deformation, low strength, cold resistance (for façade tiles), thermal stability (for interior facing tiles), and high wet thermal expansion, which together predetermine the short lifetime of the articles during use, are the basic and important drawbacks of tiles made from pastes containing 50 – 70% clay.

The basic cause is noncompletion of physicochemical processes in the products of thermal decomposition of the clays in low-temperature high-speed firing. The use of woll-

stonite allows changing the application of the clay in the tile pastes while retaining its role of binder that ensures the strength of the tile moving along the conveyor and in the roller furnace.

In low-fire ceramic pastes, for example, in red clay, wollastonite decrease air and firing shrinkage so that the articles dry “safely” and deformation and variable dimensionality are reduced. The fired articles have lower wet expansion

TABLE 3

Index	Traditional working paste	Experimental paste
Water absorption, %	0.75	0.11
	0.66	0.15
	0.73	0.16
Buckling, mm	8.2	6.4
Shrinkage, %:		
air	4.2	3.4
firing	7.8	6.7
total	12.0	10.1

and lower TCLE. During firing, wollastonite does not emit any gases, and its fibres improve the conditions for removal of gases from the fired ceramic.

In densely sintered ceramics, wollastonite can also reduce shrinkage (addition of 2–5%) and wollastonite becomes a flux at temperatures above 1100°C.

At high temperatures, wollastonite is a source of calcium and silicon, which is very important in production of glazes. In raw glazes at firing temperatures of 1150–1300°C, wollastonite is greatly preferred over chalk, since it does not release gases and consequently the surface of the article has fewer defects. Wollastonite plays the role of a nucleus former in glaze melts which is frequently used for obtaining pleasing glaze effects in the controlled cooling stage. A dull surface finish is the simplest.

The use of wollastonite as a basic component of tile pastes allows partially or totally replacing datolite concentrate and nepheline-syenite in traditional ceramic tile formulations. Wollastonite additives significantly improve the properties of tiles; they can reduce shrinkage to zero, decrease water absorption by 1.5 times, significantly increase thermal stability, increase the bending strength by 2.5 times, and increase cold resistance by 2 times, significantly improve pouring of the glaze, and increase the cohesive strength of the glaze with the ceramic. Unidimensionality of the tiles can be obtained by adding 20% wollastonite to the ceramic paste. The shrinkage will then decrease by two times, the deformability will decrease sharply, and the mechanical strength will increase. In addition, incorporation of wollastonite in the ceramic paste allows reducing the firing temperature and the sensitivity to wet thermal expansion.

Use of other GEOKOM materials in ceramics production will also increase the technical and economic and process indexes and the consumer characteristics of the ceramic ware.

MIKARB®, calcium carbonate (TU 5716-003-40705684–2001) is a white filler made of finely crystalline

marble of high natural quality in micronized form – an effective alternative to amorphous chalk; it increased the whiteness (to SIELab 99%) in a firing test, the light resistance, and improved the dielectric and strength parameters; it is distinguished by a low content of chromophores and other harmful impurities.

MITAL®, microtalc (TU 5727-001-40705684–2001) is a multifunctional, soft filler of high whiteness (up to SIELab 99%) and dispersion, with a developed flaky particle type that gives additional structure-forming and strengthening properties; after firing at approximately 1200°C, the whiteness increases and no chromophore inclusions form. Talc is added to ceramic pastes to improve their refractoriness and resistance to sharp temperature drops. Talc together with CaO increases the strength of articles at firing temperatures of 1000–1050°C, but it decreases the sintering range. Ceramic pastes containing more than 15% talc tend to absorb the glaze.

MIKAO®, calcined, dehydrated kaolin (TU 5729-011-40705684–2005), is an effective strengthening component with a combination of flaky and block particle shapes; it has elevated brightness, whiteness, and dispersion, very good electrical and thermophysical indexes, and is used in paste compositions in production of sanitary and industrial faience. Its unique properties include: when added to the paste, it reduces the intermediate product assembly time but retains the high mechanical strength of the unfired article. As a function of the features of use, the assembly time is reduced by 1.5–2 times. Kaolin can also be used in glazes and engobes. It improves the whiteness of the finished articles.

The use of modern high-quality domestic materials in ceramics production thus not only increases the quality of the articles but also significantly affects the competitiveness of the products and occupies a worthy position in the ceramic ware market.